

MELTING PROFILE, POLYMORPHIC BEHAVIOUR AND CHEMICAL COMPOSITION OF SOME SELECTED FRACTIONS ISSUED FROM THE MULTI-STEP DRY FRACTIONATION OF PALM OIL

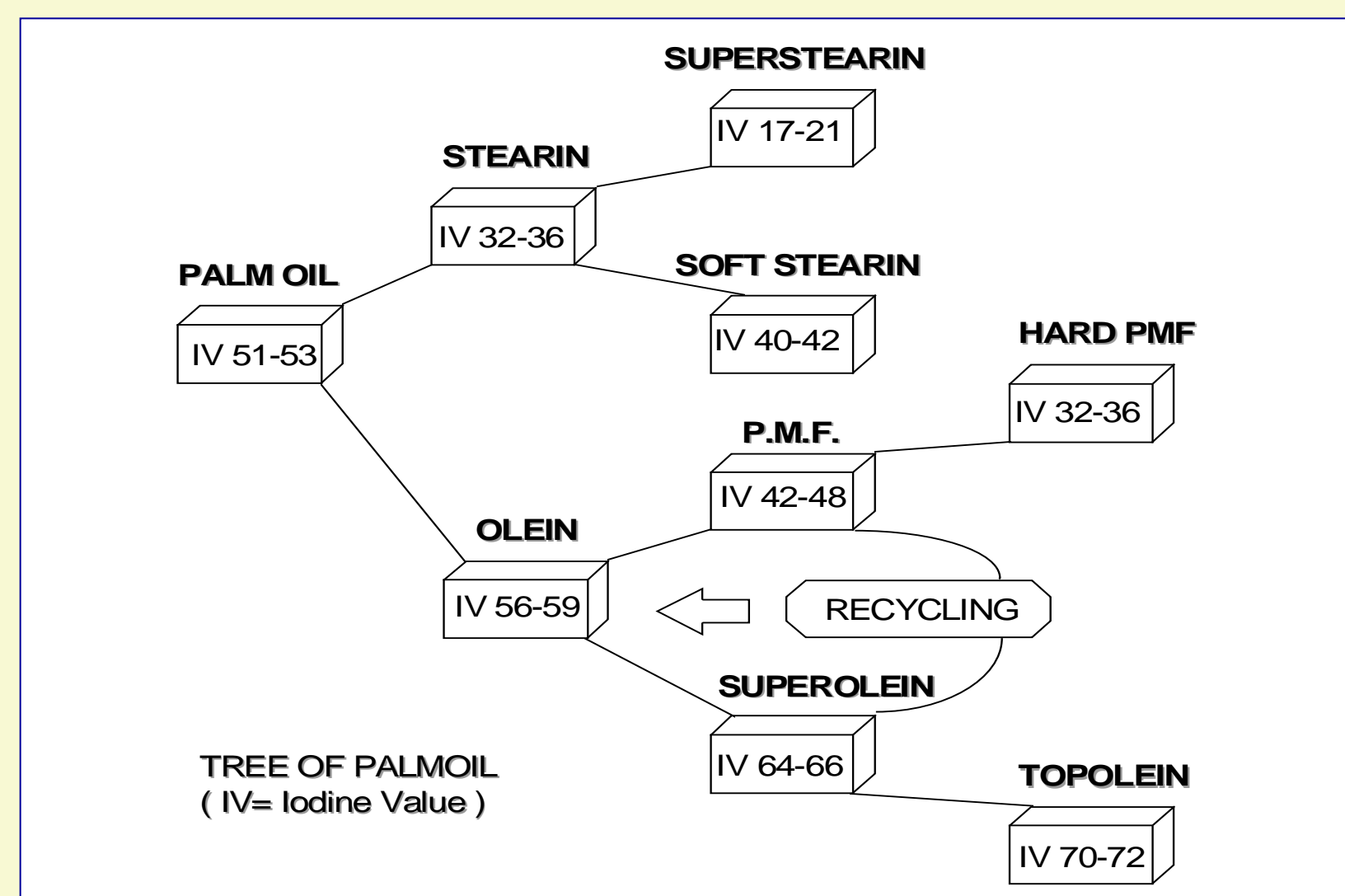
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Multistep Dry-Fractionation Tree of Palm Oil



Palm Oil is without doubt the most fractionated oil.

Multi-step dry fractionation gives rise to soft fractions (Oleins, Superoleins and Topoleins) that are used as salad, cooking and frying oils, and to harder and speciality fats.

Palm Oil is principally made of trisaturated TAG's (SSS), disaturated TAG's (SUS), monosaturated TAG's (SUU) and triunsaturated TAG's (UUU).

Limitations due to intersolubility (closely linked to polymorphism) make the separation difficult, as co-crystals are formed at each fractionation step. On

Introduction

Objectives

GOAL: Highlight the intersolubility phenomenon involved in the dry fractionation process of Palm Oil.

Several liquid and solid fractions are selected : « Liquid Route ».

Physico-chemical characteristics are examined in order to establish relationships between melting/plymorphic properties and chemical composition.

Methods:

• FAME and Iodine Value : AOCs Ce 1e-91 and Cd 1c-85.

• Cloud and Dropping point :

• TAG's composition :

• DSC :

• Powder X-Ray diffraction :



Mettler



HPLC



Melting, Cooling 25 C/min., Heating 5 C/min.



Palm Oils:

- Large range of FAME and IV (GLC) (depending on origin).
- No relationship between IV and CP.
- Large range of TAG's composition (HPLC).

SSS: 8-10%; SUS: 44-48%; SUU: 38-42%; UUU: 6-8%

• DSC :

LMP and HMP.

Total melting ΔH : 72.9 (+/-4.6) J/gr.

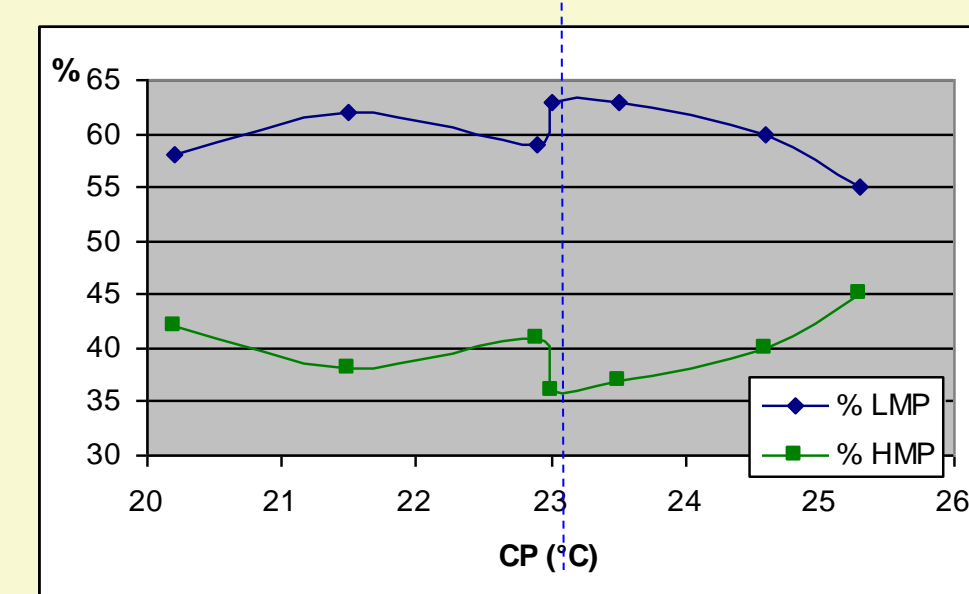
LMP, zone 5-10 C :

2 endo sub-peaks with variable intensities:
Relationship between CP and relative intensities:

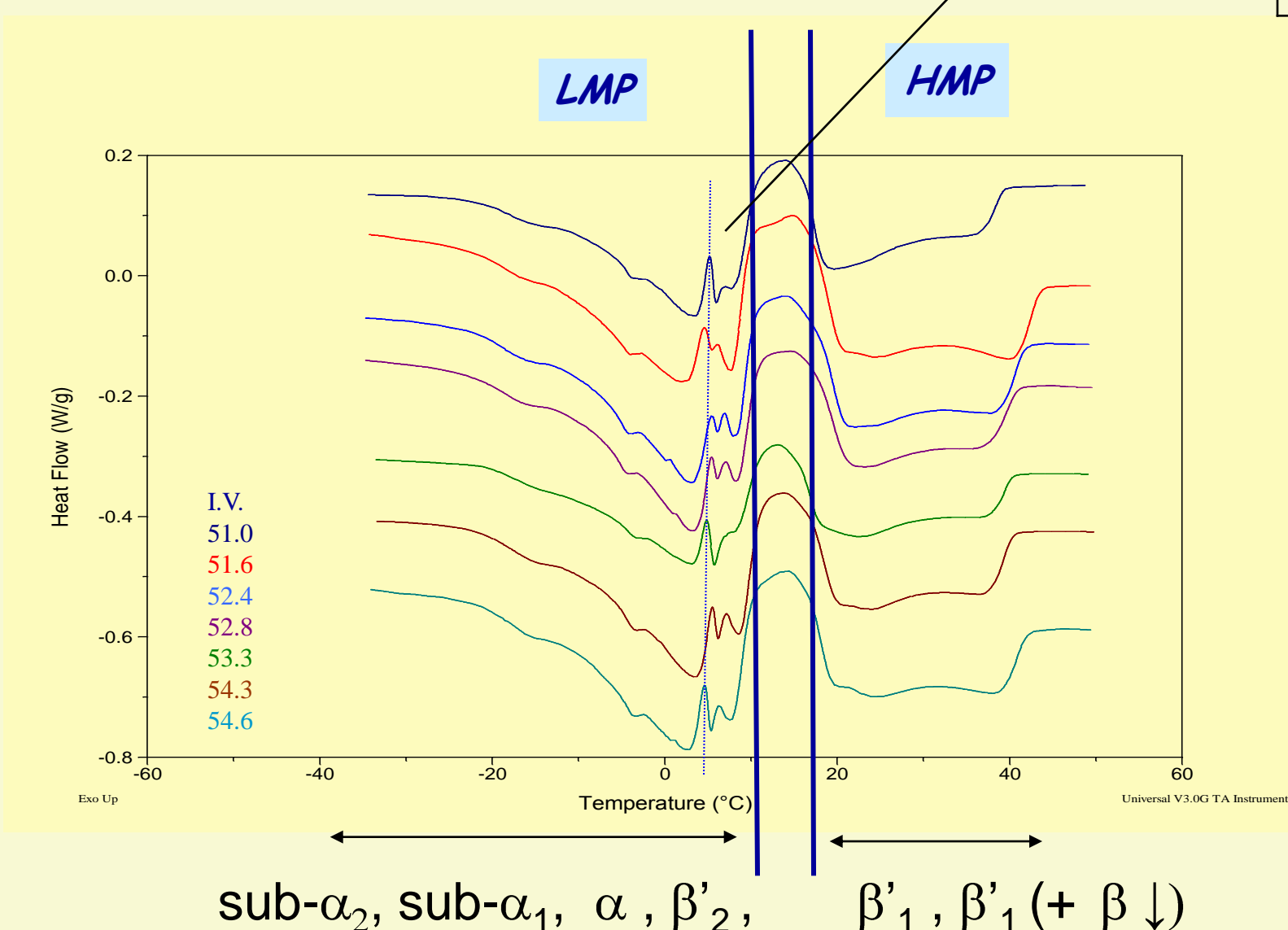
CP (°C)	20.2	21.5	22.9	23	23.5	24.6	25.3
IV	53.3	51.0	54.6	54.3	52.8	52.4	51.6
LMP (°C)	5.5 VHI	5.9 VHI	5.4 HI	6.3 HI	6.7 LI	6.2 LI	5.3 VLI
	7.9 VLI	7.7 VLI	7.7 LI	8.6 LI	8.7 HI	8.3 HI	7.6 VHI

VLI: very low intensity VHI: very high intensity LI: low intensity HI: high intensity

% LMP / % HMP: range 60%/40% :



Relationship between % LMP / % HMP and CP with « Break-point » at CP near 23 C.



See below

Palm Stearins:

- Stearin from Filter-press: IV 33.8-35.6.
- Stearin from Vacuum Filter: IV 46.8.
- TAG's composition (HPLC):

Differences between Filter-press and Vacuum Filter.

FP: SSS: 30-33%; SUS: 47-49%; SUU: 17-19%; UUU: 1-2%

VF: SSS: 17%; SUS: 46%; SUU: 32%; UUU: 5%

- DSC: total melting ΔH_{FP} : 80.0 (+/-7.5) J/gr.
- total melting ΔH_{VF} : 79.6 J/gr.

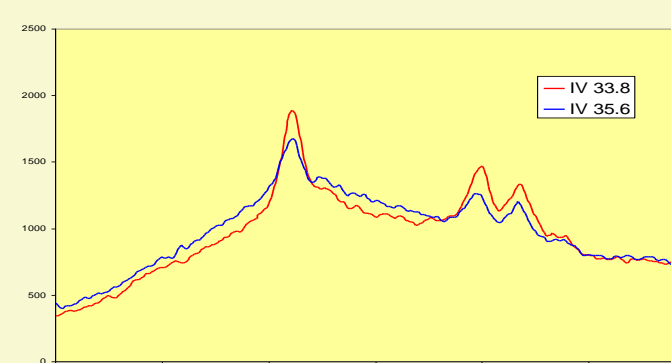
LMP, zone 5-10 C :

2 endo peaks : higher intensity of the second.

% LMP / % HMP / % VHMP:

IV	33.8	34	35.6	46.8
% LMP	26.3	27.4	29.7	50
% HMP	40.2	57.3	53.1	50
% VHMP	33.6	15.3	17.2	-
DP (C)	55.1	53.8	53.8	42

- Reduction of LMP contribution compared to Palm Oil.
- Variations in % HMP / % VHMP in relation to SSS content, dropping point, stabilisation in β and total melting ΔH .



Total melting ΔH :
IV 33.8 : 85.5 J/gr
IV 35.6 : 71.4 J/gr

Soft Stearin IV 36.2 :
Liquid fraction from Stearin IV 33.8.
DSC : total melting ΔH : 72.6 J/gr.

IV	33.8	36.2
% LMP	26.3	48.4
% HMP	40.2	46.7
% VHMP	33.6	4.9

Palm Oleins:

- Series of Oleins, Superoleins and Topolein with increased IV.
- Better relationship between IV and CP.

IV	56.4	57.7	57.8	58.4	59.5	63.6	64.6	70.6
CP (°C)	9.2	5.0	7.4	4.4	4.0	3.7	3.1	-2.5

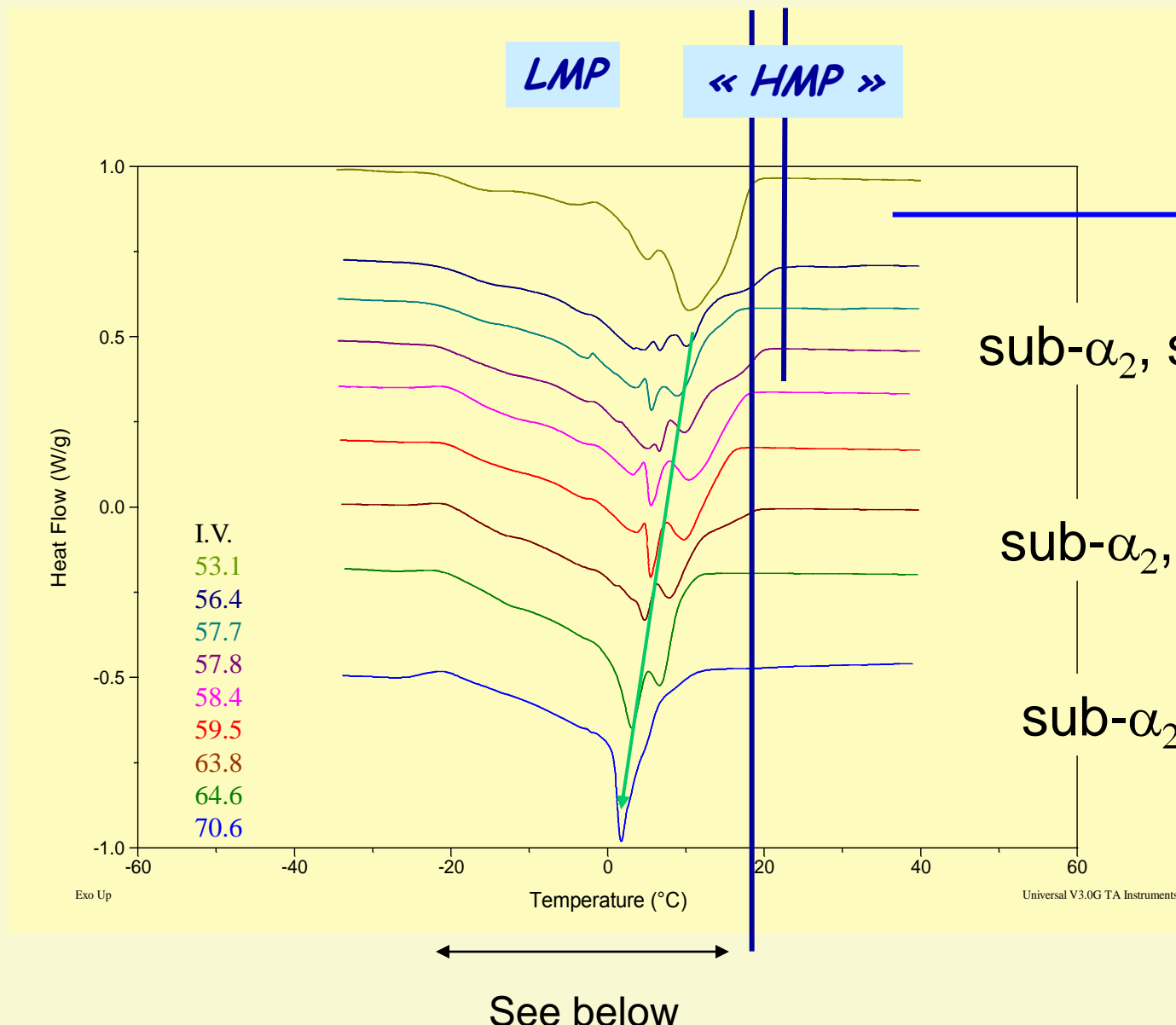
• DSC :

Only LMP

« HMP » shoulder is nevertheless observed for lower IV oleins (higher CP).

Three sub-peaks in LMP for oleins, two for superoleins and one for topolein.

Total melting ΔH : 64.0 (+/- 2.0) J/gr (54.0 J/gr for Topolein).



See below

Olein IV 53.1; CP 6.5 C :
Liquid fraction from Hard PMF IV 35.1.

sub- α_2 , sub- α_1 , α , β'_2 , β'_1
sub- α_2 , sub- α_1 , α , β'_2
sub- α_2 , sub- α_1 , α

• TAG's composition :

	IV	56.4	57.7	59.5	63.8	64.6	70.6
OOO	4.2	4.3	5.8	6.2	5.7	12.0	
POO	25.5	26.5	31.9	31.3	33.4	35.1	
POP	30.7	29.3	28.9	22.8	17.8	6.5	
PPP	1.2	0.5	0.0	0.0	0.0	0.0	
SSS	1.5	0.5	0.0	0.0	0.0	0.0	
SUS	49.1	47.7	44.0	37.8	34.6	16.6	
SUU	42.6	45.4	47.5	53.0	56.3	65.6	
UUU	6.7	6.4	8.5	9.2	9.1	17.8	

3 sub-peaks in LMP 2 sp 1 sp

Palm Mid Fractions:

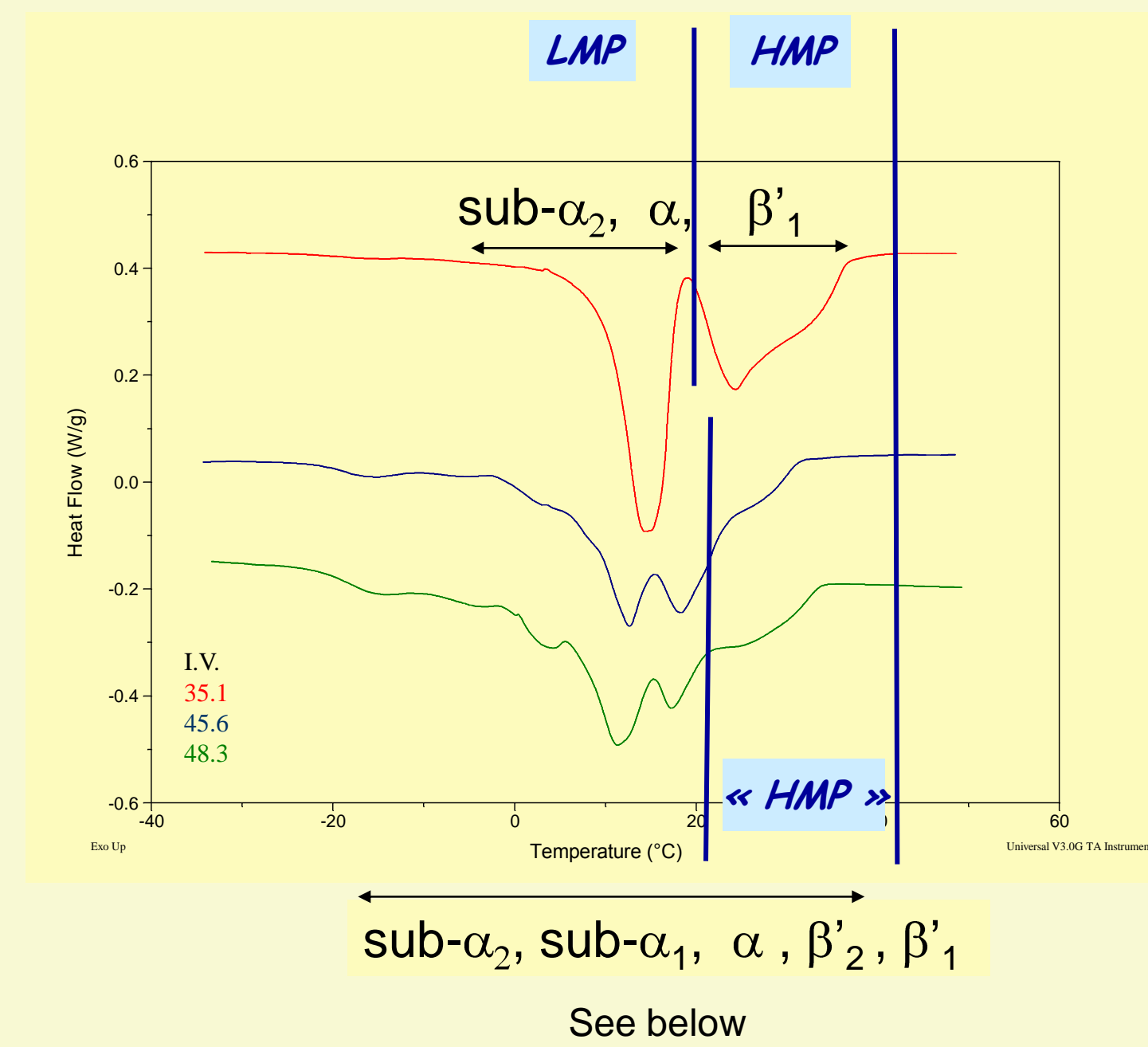
- Two Soft PMF and one Hard PMF.

IV	48.3	45.6	35.1
DP (°C)	30.2	28.3	35.6

• DSC:

Soft PMF's: LMP + « HMP » shoulder.

Hard PMF: LMP and HMP.



See below

Soft PMF's :

(IV 48.3) :

LMP : 2.9 C, 11.7 C, 16.9 C.

« HMP » : 26.2 C.

Total melting ΔH : 74.5 J/gr.

(IV 45.6) :

LMP : 12.6 C, 18.2 C.

« HMP » : 26.2 C.

Total melting ΔH : 67.6 J/gr.

Hard PMF:

LMP: 14.5 C

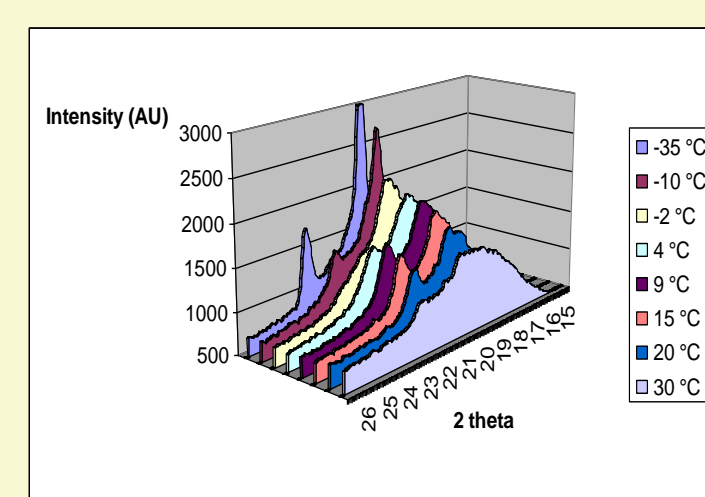
HMP : 24.4 C + shoulder at 33.6 C

% LMP / % HMP : 60% / 40%

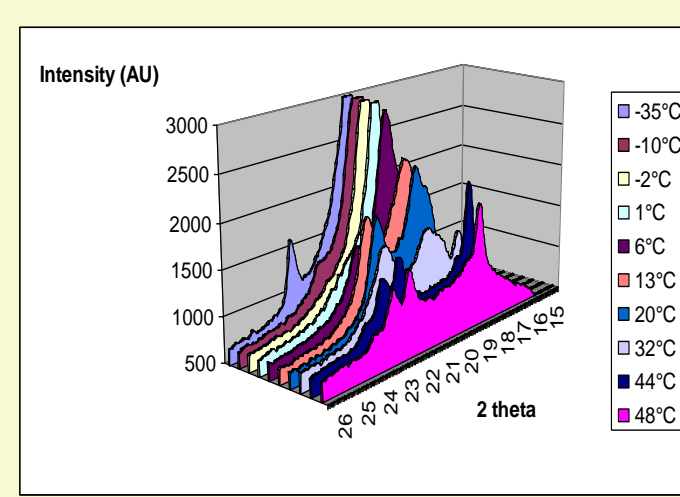
Total melting ΔH : 76.4 J/gr.

• TAG's composition :

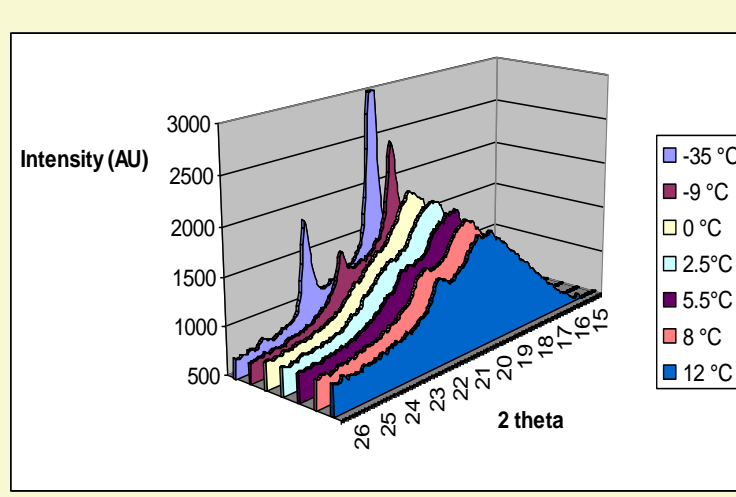
IV	48.3	45.6	35.1
OOO	3.5	2.5	1.7
POO	18.0	14.7	5.6
POP	39.7	49.5	65.5
PPP	2.1	1.3	3.0
POS	13.2	9.0	10.3
PPS	0.7	0.3	0.7
SOS	1.9	1.4	1.4
PSS	0.0	0.0	0.1
SSS	2.8	1.6	3.8
SUS	63.5	70.6	85.4
SUU	28.8	24.0	8.6
UUU	4.9	3.8	2.1



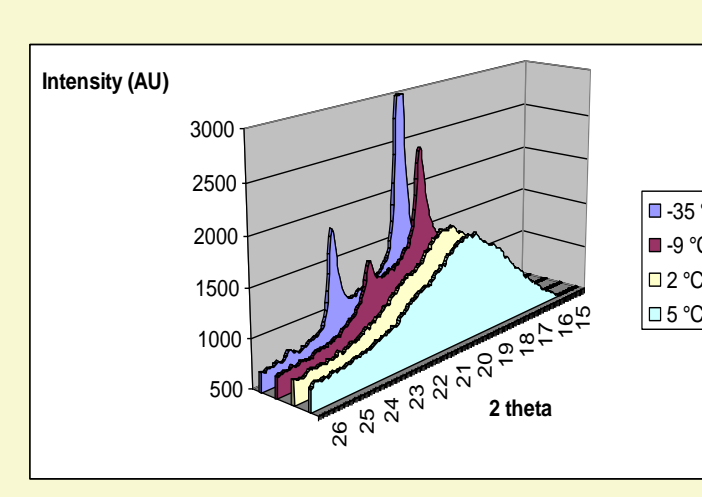
Palm Oil



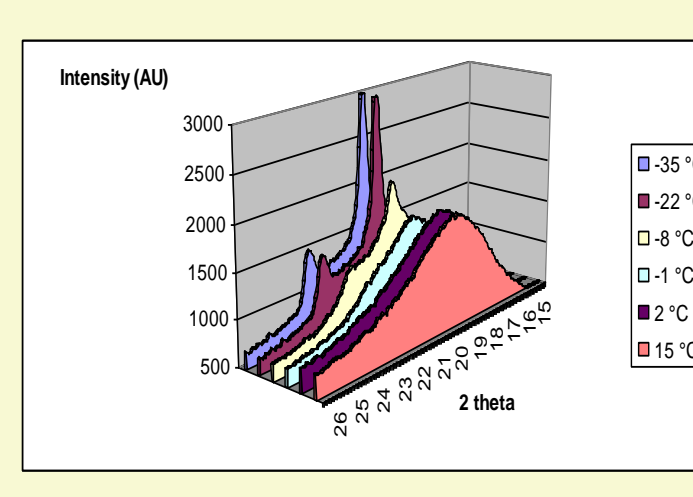
Palm Stearin



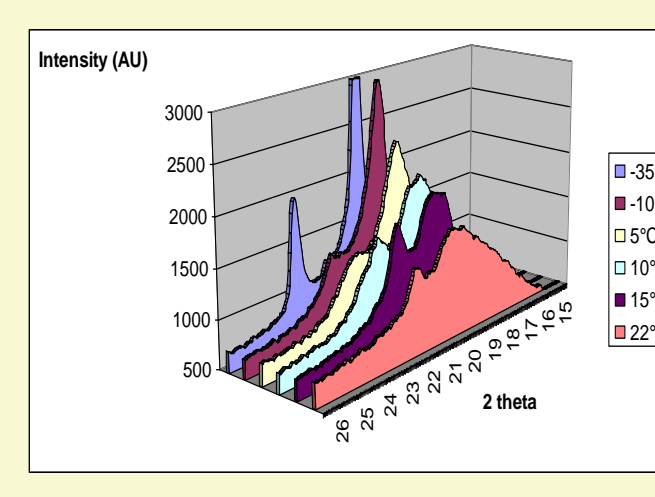
Palm Olein



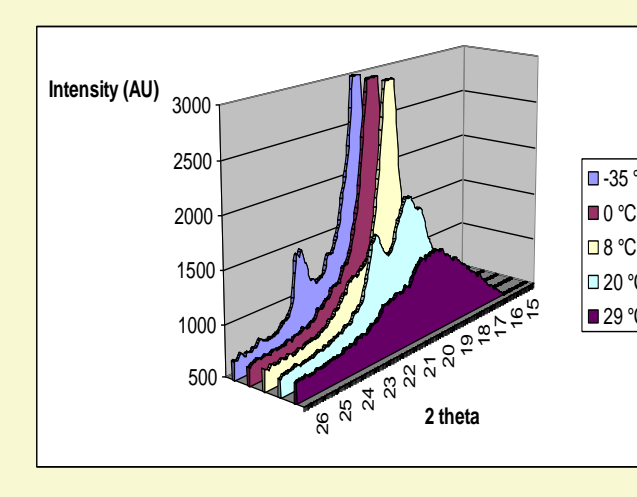
Palm Superolein



Palm Topolein



Soft PMF



Hard PMF

Conclusions:

Palm Oils : Two main populations of intersoluble co-crystals. LMP = sub- α_2 , sub- α_1 , α , β'_2 . HMP = β'_1 , β'_1 + β (\downarrow). LMP = UUU + SUU. HMP = SUS + SSS.

Palm Stearins : Three main populations of intersoluble co-crystals. LMP = sub- α_2 , sub- α_1 , α , β'_2 . HMP = β'_1 . VHMP = β . LMP = UUU + SUU. HMP = SUS. VHMP = SSS.

Palm Oleins : One main population of intersoluble co-crystals with sub-populations. LMP = sub- α_2 , sub- α_1 , α , β'_2 , β'_1 (\downarrow). LMP = UUU + SUU + SUS. 3 sub-populations below IV 60. 2 sub-populations for IV 63-65. 1 sub-population for IV +/- 70. Relationship with SUS content.

Palm Mid Fractions : Soft PMF : One main population of intersoluble co-crystals with sub-populations : 3 or 2 (SUS + SUU and UUU, \downarrow) + HMP shoulder (SUS + SSS).

Hard PMF: Two main populations of intersoluble co-crystals : LMP (SUS) + HMP (SUS + SSS).